REMARKS/ARGUMENTS

In view of the remarks and arguments below, Applicant believes the pending application is in condition for allowance.

I. Status of the Claims

Claims 1 and 3-27 were previously pending.

Claims 2, 28, and 29 were previously canceled without prejudice to or disclaimer of the subject matter contained therein.

Claims 7, 8, 10, 13, 21, 22, and 26 are canceled in this Amendment without prejudice to or disclaimer of the subject matter contained therein.

Claims 1, 14, and 16 are amended as follows.

Claims 1 and 16 are amended to change the range of the variable m recited from "2 to 100" to "10 to 100" (i.e., "m represents an integer from [[2]]10 to 100"). Support for the amendments can be found, for example, in canceled claim 8 for claim 1, and in canceled claim 22 for claim 16. No new matter is introduced by the amendments.

Claims 1 and 16 are further amended to recite that "the copolymer exhibits a microphase separated structure." Support for the amendments can be found, for example, in canceled claim 13 for claim 1, and in canceled claim 26 for claim 16. No new matter is introduced by the amendments.

Claim 14 is amended to place the Markush language recited in proper format (i.e., "selected from [[a]]the group consisting of"). No new matter is introduced by the amendment.

Upon entry of this Amendment, claims 1, 3-6, 9, 11, 12, 14-20, 23-25, and 27 are pending and at issue.

II.   Withdrawal of Final Office Action Dated April 9, 2008

Applicant appreciatively thanks Examiner Bernshteyn for withdrawing the Final Office Action dated April 9, 2008, and for issuing in its place the currently outstanding Non-Final Office Action dated May 13, 2008.[1]

III.   Claim Rejections under 35 U.S.C. § 103(a)

Claims 1 and 3-27 are rejected under 35 U.S.C. § 103(a) as unpatentable over a journal article authored by Khan et al.[2] ("Khan") in view of United States Patent No. 5,196,484 to Giles et al. ("Giles"). The Examiner states that Khan in combination with Giles renders the claims obvious.

Claims 7, 8, 10, 13, 21, 22, and 26 have been canceled, rendering the rejections of these claims moot.

For the pending claims 1, 3-6, 9, 11, 12, 14-20, 23-25, and 27, Applicant respectfully traverses the rejections at least for the reasons that: (A) the present invention achieves unexpected, superior results that cannot be predicted from Khan and Giles, either alone or in combination; and (B) regardless of the results achieved, one of ordinary skill in the art would not be motivated to combine Khan and Giles.

A.   Unexpected, Superior Results Achieved by the Present Invention

The Examiner's rationale for establishing a *prima facie* case of obviousness relies on the alleged close structural similarity between the copolymers of the present invention and those suggested by the combination of Khan and Giles.[3] However, "[a] *prima facie* case of obviousness based on structural similarity is rebuttable by proof that the claimed compounds possess

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[1] Non-Final Office Action dated May 13, 2008, page 2, lines 13-14.

[2] Ishrat M. Khan, Daryle Fish, Yadollah Delaviz, and Johannes Smid, "ABA Triblock Comb Copolymers with Oligo(Oxyethylene) Side Chains as Matrix for Ion Transport," *Makromolekular Chemie*, 190, 1069-78 (1989).

[3] "When chemical compounds have very close structural similarities and similar utilities, without more a *prima facie* case [of obviousness] may be made." Non-Final Office Action dated May 13, 2008, page 3, lines 6-8 (quoting *In re Wilder*, 563 F.2d 457, 461 (CCPA 1977)).

unexpectedly advantageous or superior properties."[4] Applicant respectfully submits that such proof was previously presented.

Specifically, Applicant previously presented evidence that the claimed arrangement of copolymer block chains was nonobvious based on their unexpectedly superior conductive properties compared to the prior art.[5] The room temperature conductivities of copolymer-$LiClO_4$ electrolyte complexes disclosed by Khan range from 0.7 to $1.2 \times 10^{-6} \ \Omega^{-1} \cdot cm^{-1}$ (Table 4). In contrast, experimental data show that the presently claimed copolymer-$LiClO_4$ electrolyte complexes exhibit conductivities that are greater by more than an order of magnitude — from 5×10^{-5} to $3.8 \times 10^{-4} \ \Omega^{-1} \cdot cm^{-1}$ (Examples 1-4 of the Specification).

In response, the Examiner stated that "it is worth to mention that Khan discloses that the ion conduction can reach values of $10^{-4} \ \Omega^{-1} \cdot cm^{-1}$ at 70°C, depending on salt and styrene content (abstract)."[6] However, Khan states that "[a]ddition of dimethyltetraethyleneglycol (2,5,8,11,14-pentaoxapentadecane) enhances the ion conduction which can reach values of $10^{-4} \ \Omega^{-1} \cdot cm^{-1}$ at 70°C, depending on salt and styrene content" (Abstract; emphases added).

Adding DMTEG,[7] a plasticizer, to a polymer electrolyte and increasing temperature increases the conductivity of the electrolyte (somewhat at the expense of the mechanical properties of the polymer due to the plasticizer).[8] In contrast, Applicant measured the conductivities of the presently claimed solid polymer electrolytes without DMTEG and at room temperature.

Accordingly, conductivity measured (1) after the addition of dimethyltetraethylene glycol (DMTEG) and (2) at a much higher temperature does not relate to the conductivity measured by Applicant, and fails to show that the results of the present invention were ordinary or expected. The

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[4] MPEP § 2144.09, VII, first sentence.

[5] Amendment filed on May 30, 2007, pages 10-11.

[6] Final Office Action dated August 23, 2007, page 6, lines 4-6.

[7] The acronym "DMTEG" is a shorthand notation for dimethyltetraethyleneglycol (2,5,8,11,14-pentaoxapentadecane). Khan, p. 1077, line 14.

[8] Khan, page 1077, second paragraph and Table 3.

nature of Applicant's results should only be compared to the data from Khan at room temperature and in the absence of DMTEG — from 0.7 to 1.2×10^{-6} $\Omega^{-1} \cdot cm^{-1}$ (Table 4).

Moreover, neither Khan nor Giles suggests that rearranging the block chains of Khan would improve conductivity, let alone to the degree discovered in the present invention. In fact, as previously argued,[9] Khan teaches away from this rearrangement. Khan states that increasing the amount of the polystyrene block will lower the conductivity. Accordingly, the conductivities of the presently claimed solid polymer electrolytes were not only superior to the those of the prior art but also unexpected. *KSR Int'l Co. v. Teleflex Inc.*, 127 S. Ct. 1727, 1740 (2007) ("when the prior art teaches away from combining certain known elements, discovery of successful means of combining them is more likely to be nonobvious").

At least for the reasons stated above, Applicant respectfully submits that Khan in view of Giles does not render any of claims 1, 3-6, 9, 11, 12, 14-20, 23-25, and 27 obvious, and respectfully requests that the rejections of these claims be withdrawn.

B.   Lack of Motivation to Combine Khan and Giles

Further, according to the Examiner, the only difference between Khan and the present invention is the sequence of the block chains A, B, and C.[10] The Examiner's position is that it would have been obvious to one having ordinary skill in the art to place the **A** block in the middle of the Khan **ABA** block (i.e., to form a **BAB** block copolymer) as taught by Giles in order to reduce ambient temperature crystallization.[11]
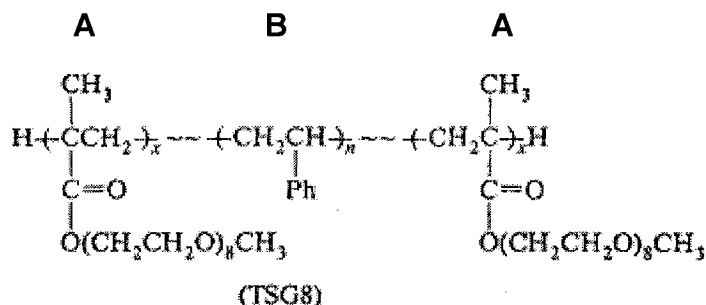
However, the motivation cited by the Examiner ("to reduce ambient temperature crystallization") does not relate to block chain rearrangement. Giles teaches that short oxyalkane sequences, i.e., low values of m, are desirable to reduce ambient temperature crystallization.

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[9] Amendment filed on May 30, 2007, page 9, last paragraph.

[10] Non-Final Office Action dated March 8, 2007, page 4, lines 1-3.

[11] Non-Final Office Action dated March 8, 2007, page 5, lines 3-8.

Preferably, the value should lie between 7 and 17.[12] Based on this teaching, a skilled artisan that wished to reduce ambient temperature crystallization would use short oxyalkane sequences. Therefore, a skilled artisan that wished to reduce ambient temperature crystallization in the Khan **ABA** block copolymer, namely,

$$
\begin{array}{ccc}
\mathbf{A} & \mathbf{B} & \mathbf{A}
\end{array}
$$

$$
\begin{array}{ccc}
CH_3 & & CH_3 \\
| & & | \\
H\!-\!\!(\!CCH_2\!)_{\!x}\!-\!\!-\!(\!CH_2CH\!)_n\!-\!\!-\!(\!CH_2C\!)_x\!H \\
| & | & | \\
C\!=\!O & Ph & C\!=\!O \\
| & & | \\
O(CH_2CH_2O)_4CH_3 & & O(CH_2CH_2O)_8CH_3
\end{array}
$$

(TSG8)

would shorten the oxyethylene side chains. Contrary to the Examiner's contention, this would not result in a rearrangement of the block chain sequence; it would only affect the length of the side chains in the **A** blocks.

At least for this reason, Applicant respectfully submits that one of ordinary skill in the art would not have been motivated at the time of the present invention to rearrange the Khan **ABA** block copolymer.

In addition, while the Examiner states that the "instantly claimed block chain A also could contain low values of m beginning with number 2,"[13] the block chain A recited in claims 1 and 16 as amended no longer contains low values of m. (The remaining pending claims 3-6, 9, 11, 12, 14, and 15 depend from claim 1, and claims 17-20, 23-25, and 27 from claim 16.) Also, one of ordinary skill in the art would know that having long oxyalkane sequences would make it difficult for the living anion polymerization process during synthesis to proceed smoothly.

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[12] Giles, column 5, lines 8-15.

[13] Non-Final Office Action dated May 13, 2008, page 3, lines 17-18.

For this additional reason, Applicant respectfully submits that one of ordinary skill in the art would not have been motivated to rearrange the Khan block copolymers to arrive at the present invention.

Further, while the Examiner states that Giles discloses ABA triblock copolymers, Giles neither discloses nor teaches examples demonstrating that ABA triblock copolymers with a microphase separated structure can be prepared actually. Giles discloses the so-called "iniferter" method as a method to be adopted for synthesizing such triblock copolymers.[14] The term "iniferter" is an abbreviation of "initiator-transfer agent-terminator,"[15] and the iniferter method is one of living radical polymerization methods.

Although the iniferter method allows the radical polymerization to take place in a living manner, the control of the polymerization is quite difficult. Therefore, the iniferter method tends to broaden the molecular weight distribution of the resulting polymers and cause termination of the polymerization or dimerization. For this purpose, Applicant submits an article taken from pages 121-126 of the book titled "Radical Polymerization Handbook" as Exhibit A, and an English translation of the article as Exhibit B. The article was authored by T. Otsu. In introducing the iniferter method, Giles cites a journal article also co-authored by T. Otsu.[16] The Radical Polymerization Handbook was first published in 1999.

In contrast to the iniferter method, it is well known to one having ordinary skill in the art that the formation of a microphase separated structure requires a narrow molecular weight distribution and a controlled molecular weight.

Accordingly, Applicant respectfully submits that it would not have been obvious at the time of the present invention for one having ordinary skill in the art to obtain a copolymer having a microphase separated structure by incorporating polymethacrylate with an oligo(oxyethylene) block

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[14] Giles, column 7, lines 9-11.

[15] Exhibit B, page 3, lines 8-9.

[16] Giles, column 7, lines 9-11.

- 14 -

in the middle in accordance with the methods disclosed or taught by Khan or Giles to arrive at the subject matter of claim 1 or 16. The remaining pending claims depend from claim 1 or 16.

At least for the reasons stated above, Applicant respectfully submits that Khan in view of Giles does not render any of claims 1, 3-6, 9, 11, 12, 14-20, 23-25, and 27 obvious, and respectfully requests that the rejections of these claims be withdrawn.

CONCLUSION

In view of the foregoing, it is believed that pending claims 1, 3-6, 9, 11, 12, 14-20, 23-25, and 27 are in immediate condition for allowance and it is respectfully requested that the application be reconsidered and that all pending claims be allowed and the case passed to issue.

If there are any other issues remaining which the Examiner believes could be resolved through a Supplemental Response or an Examiner's Amendment, the Examiner is respectfully requested to contact the undersigned at the telephone number indicated below.

Dated: September 12, 2008

Respectfully submitted,

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- 15 -

Exhibit A

ラジカル重合ハンドブック
── 基礎から新展開まで ──

←── 監修者

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第4節　イニファータ法によるリビングラジカル重合

1. はじめに

1956年，Szwarc[1]はナフタレンナトリウムによるスチレンの重合からリビングポリマーが生成することを報告した。このリビング重合の発見は，高分子の一次構造（分子量，分子量分布，末端基構造など）の制御やテレケリック・ブロック・グラフトポリマーの設計合成に大きなインパクトを与えた。以来，リビング重合が構造制御の原点と考えられ，1970年頃からアニオン重合，カチオン重合，ラジカル重合，開環重合，配位重合，メタセシス重合，重縮合などのリビング化が達成され，さらにグループ移動重合，イモータル重合，新規遷移金属触媒重合などのリビング系が報告された[2-5]。

このうち，ラジカル重合以外のリビング系では，新規触媒系の開発によって達成されたが，ラジカル重合は，電気的に中性で短寿命のフリーラジカルを中間体（成長活性種）とする連鎖反応で進むため，通常の触媒（開始剤）によるリビング化は期待できない。また，フリーラジカルには，DPPHやフェルダジルなどのように長寿命のラジカルも存在するが，これらは重合の禁止剤として機能し，安定ラジカルと呼ばれて，ここでいうリビングラジカルではない。リビングラジカル重合化とは，短寿命のラジカルをいかにして長寿命化するかということになる。それには，成長ラジカルの失活（停止）を防ぐため，その易動度をゼロにすることが考えられ，乳化系，沈殿系，凍結系，ミクロゲル系，高粘度媒体中などでの重合が試みられたが，ESRで成長ラジカルは検出されるものの，重合はリビング的に進行しなかった[2-4]。

このように考えてくると，均一系リビングラジカル重合を構築するためには，全く新しい発想の導入が必要であった。1982年，大津らはラジカル重合で生成するポリマーの末端構造を制御し，設計するためのイニファータ法[9]ならびに均一系リビングラジカル重合モデル[10]を提案した。今日では，イニファータやそれを用いたリビングラジカル重合という

用語は広く用いられているが，誤解されていることも多い。本稿では，これらの基本的な考え方を整理するとともに，最近の研究との関係についても述べる。なお，詳細は総説[2-6]などを参照していただきたい。また，ブロック・グラフトポリマーの設計合成については別稿[13]でも述べる。

周知のごとく，ラジカル重合は多数のビニル系モノマーの高分子化に有効で，大量の汎用ビニル系ポリマーが工業生産されている。しかし，分子量分布や一次構造（とくに立体構造）の制御はあまり進んでいない。近年来，精密重合の気運の高まりから，リビングラジカル重合などによるラジカル重合の構造解析やESR・パルスレーザー重合による成長ラジカルの精密構造・速度解析などが激しく展開されている。ラジカル重合のメリットを生かした精密重合法としての進展が待たれている[6][11]。

2. イニファータとは

ラジカル重合の停止は，再結合と不均化で起こり，連鎖移動が起こらない限り，それぞれ両末端と片末端に開始剤切片が結合したポリマーが生成する。両反応の起こりやすさは主としてモノマーの構造で決められているため，ポリマーの末端基構造を制御することは難しい。しかし，開始剤への連鎖移動と一次ラジカル停止のいずれか，または両方を起こしやすい開始剤（R-R）を用いた場合には，両末端に開始剤切片（R）が結合したポリマーが生成することになる。

$$R-R + nM \longrightarrow R-(M)_n-R \qquad (1)$$

この反応は，開始剤へのモノマーの挿入反応にほかならない。このような機能を持つ開始剤に対してイニファータ（initiator-transfer agent-terminator の略）と名づけられた。そのルーツは，Gombergによるトリチルラジカル（1）がその二量体（2）との解離平衡にあること，これにビニルモノマーが挿入される（3）というMarvelらの研究であろう。式(2)は，次項で述べるリビングラジカル重合モデル

のルーツでもある。またテロメル化におけるテロゲン（連鎖移動剤）の機能もモノマー挿入反応で起こる。例えば，CCl₄をテロゲンとした場合には式(3)で進む。

$$2 \quad 1 \quad 3 \tag{2}$$

$$Cl_3C-Cl+nM \longrightarrow Cl_3C-(M)_n-Cl \tag{3}$$

1982年，イニファータ法を提案したときに用いたイニファータは，フェニルアゾトリフェニルメタン（4），テトラフェニルエタン類（X＝C₂H₅，CN，OC₆H₅など）（5），テトラエチルチウラムジスルフィド（6）のようなイオウ化合物である[1][7]。前二者は熱，後者は光イニファータとして機能する。

$$4 \quad 7 \tag{4}$$

$$5 \quad 8 \tag{5}$$

$$(C_2H_5)_2NCS-SCN(C_2H_5)_2+nM \longrightarrow$$
$$6$$

$$(C_2H_5)_2NCS-(M)_n-SCN(C_2H_5)_2 \tag{6}$$
$$9$$

ここで，生成したポリマー（4～6）の末端基は，さらに熱あるいは光イニファータ（高分子イニファータと呼ぶ）として働くことが見いだされた。この場合のイニファータ結合は，それぞれC—C（トリチル），C—C（ジフェニルメチル），C—S結合である。最近，注目されているスチレン／ニトロキシドリビング系では，C(C₆H₅)—ON₂結合である[11]。反応はこれにモノマーの挿入反応で進む。このような高分子イニファータにより第二モノマーの重合を行うことによって種々のブロックポリマーが生成することになる。例えば9から10が得られる。

$$9+mM' \xrightarrow{h\nu} \quad 10 \tag{7}$$

このように，種々のイニファータを用いることにより官能性，テレケリック，ブロック，グラフトポリマーなどが設計合成されることになる（4.項参照）。

3. 均一系リビングラジカル重合モデル

式(2)，(4)～(7)に示したように，イニファータ結合にモノマーが挿入して進む場合には，このラジカル重合はリビング的に進行することになる。モノマーの挿入は，イニファータ結合の解離，モノマーの付加，一次ラジカル停止（PRT）で起こる。1982年，提案したイニファータを用いて均一系リビングラジカル重合モデルを式(8)に示す。ここで，CTはイニファータ結合（C—B）への連鎖移動で，この反応が起こっても式(8)のモデルには関係しない。

$$10 \quad 11 \quad 12 \tag{8}$$

ここで，10のC—B結合の解離により11と12が生成する。11は成長ラジカルでMと反応し，12は原則として開始能を持たないが，11とのみ反応（PRT）し10に戻る。分かりやすく書くと，式(9)となる。

$$10 \quad 11 \quad 12$$
$$10 \quad 11 \tag{9}$$

したがって，10のC—B結合は11の休止（dormant）種と見られる高分子イニファータである。このモデルに従って重合が起こるなら分子量は時間（重合率）とともに増大（図1）し，生成ポリ

るることに
ラフトポ
(4.項参

ミデル

ータ結合
ラジカル
Eノマー
マーの付
1982年,
ングラジ
はイニ
Eの反応

$I_2 = CHX$
$\overline{RT/CT}$

$H_2 = CHX$
$\overline{RT/CT}$

(8)

11 と 12
し, 12
つみ反応
式(9)と

(9)

の休止
ータであ
分子量は
E成ポリ

<!-- 図1 -->
[St]＝6.9mol·ℓ^{-1}
[21]＝7.8×10^{-3}mol·ℓ^{-1} (●,■)
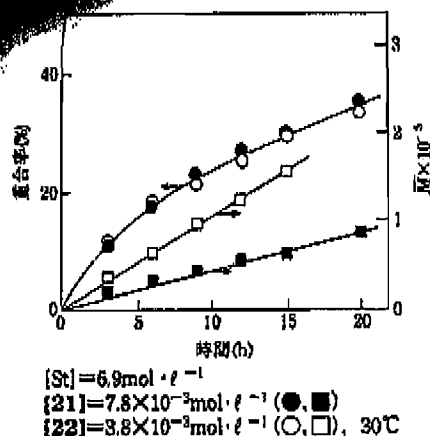[22]＝3.8×10^{-3}mol·ℓ^{-1} (○,□), 30℃

図1 21および22を用いたStの光重合における時間-重合率および時間-分子量の関係

マーはブロックポリマーなどの合成に用いられる。4〜6をイニファータとしたスチレン（St）やメタクリル酸メチル（MMA）のリビングラジカル重合がこの例である。

これら重合を，リビングイオン重合と比較すると，生成ポリマーの分子量の増大，ブロックポリマーの生成では一致するが，分子量分布は単分散に近づかない（図2参照）。イオン重合では開始が成長に比して速やかに起こり，二分子停止も起こらないのに対し，ラジカル重合では開始は遅く，成長は速く，11の濃度を高めると二分子停止も容易に起こること

<!-- 図2 -->
時間/h	$\overline{M}_w/\overline{M}_n$
3	2.1
6	2.1
10	2.3
15	2.9
20	2.9

溶出時間(min)

[21]＝7.3×10^{-3}mol·ℓ^{-1}
バルク重合, 30℃
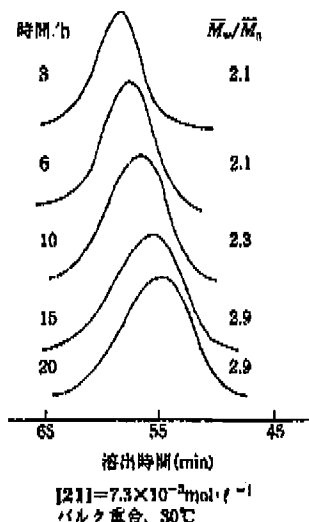
図2 21による光重合で得られたポリスチレン(St)のGPC曲線

とになる。このため，ラジカル反応で構造制御を考えるとき，まず11の選択性を高めるために低い温度で反応を行うのが原則である。4や5のような熱イニファータでは，70-100℃で重合を誘起するため，11とB•中のベンゼン核への置換が副反応として起こり，リビング性は低下する。6のようなイオウ系光イニファータ（～C-S）では，室温で重合が進行するため副反応は避けられるものの，式(9)の11とMの反応（成長）に比して11とB•との反応（PRT）が遅いために，成長が連鎖的に進み，単分散に近いポリマーは得られない。

1994年，Georgesら[11]は，2,2,6,6-テトラメチルピペリジニル-1-オキシル（TEMPO），過酸化ベンゾイル，Stを95℃で3.5h加熱し，ついで123℃，69h重合させることによって$M_w/M_n=1.27$のポリStを合成した。第一段の反応でイニファータ結合～C(C_6H_5)-ON、が生成し，この結合にStモノマーが挿入されて進む。この結合は高い結合解離エネルギーを持つとはいえ，123℃，69hの反応は全く予想を超えるものであったが，構造的に副反応が阻害されており，かつB•は安定ラジカル（禁止剤）であるため，上記リビングラジカル重合モデルの条件が満たされ，ラジカル重合で単分散に近いポリマー（ただし，ポリSt）の生成を可能にしたと考えられる。現在，多くの研究者によって研究されており，新たなる展開を期待したい[6]〜[8]。
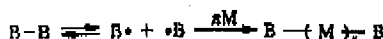
4. イニファータ法とその機能的分類と応用

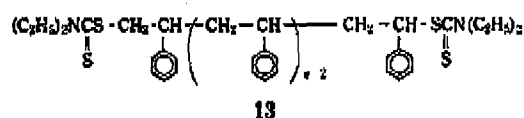イニファータを用いて高分子の末端基構造の設計ならびにブロックポリマーなどを設計合成する方法はイニファータ法と呼ばれる。ここでは，われわれが研究してきたイオウ系光イニファータ法を中心に述べる[2]〜[1]。

イニファータは機能的に二つのタイプ，A-B型とB-B型に分類される。

$$\text{A-B} \rightleftharpoons \text{A•} + \text{•B} \xrightarrow{nM} \text{A}\text{—}(\text{M})_n\text{—B}$$
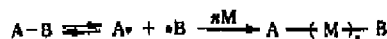
ここで，A•は高反応性のラジカル，B•は非（または低）反応性ラジカルで，それぞれ開始と停止に寄与する。

$$\text{B-B} \rightleftharpoons \text{B•} + \text{•B} \xrightarrow{nM} \text{B}\text{—}(\text{M})_n\text{—B}$$

ここで，B•は低反応性ラジカルで開始と停止の双方に関与する。いま，B-B型のジスルフィド6を光イニファータとして St を重合した場合には，13 のポリマーが生成する。

$$\text{(C}_2\text{H}_5\text{)}_2\text{NCS-CH}_2\text{-CH}\!\!-\!\!\text{CH}_2\text{-CH}\!\!-\!\!-\!\!\text{CH}_2\text{-CH-SCN(C}_2\text{H}_5\text{)}_2$$

13

13 の両末端には，イニファータ基が結合しているが，一つ手前のモノマー単位まで考えると末端基構造 14, 15 は同じではなく，光解離の結合位置も異なる。すなわち，

右 (h) 末端基：

$$\sim \text{CH}_2\text{-CH}\!\!-\!\!\text{SCN(C}_2\text{H}_5\text{)}_2 \longrightarrow \sim \text{CH}_2\text{-CH} \bullet\bullet \text{SCN(C}_2\text{H}_5\text{)}_2$$

14　　　**16**　　　**17** (10)

左 (t) 末端基：

$$\sim \text{CH-CH}_2\!\!-\!\!\text{SCN(C}_2\text{H}_5\text{)}_2 \longrightarrow \sim \text{CH-CH}_2\text{S} \bullet\bullet \text{CN(C}_2\text{H}_5\text{)}_2$$

15　　　**18**　　　**19** (11)
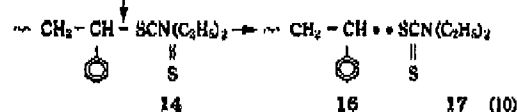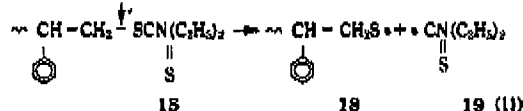
矢印の結合で解離すると，14 末端からは成長ラジカル 11 であるポリスチリルラジカル 16 を再生し，同時に低反応のチイルラジカル 17 を生成する。しかし，15 末端からは低反応性のポリフェニルエチ

ルチイルラジカル 18 と高反応性の炭素ラジカル 19 が生成し，11 は再生されない。これでは，末端構造設計には適当ではなく，必ず 11 が再生する A-B 型イニファータを使用しなければならない。一般に，A-B 型の方がリビング性およびブロック効率は高い。

表1に，イニファータの機能，応用面からの分類を示す。

5. イニファータによるリビングラジカル重合の特徴

5.1 熱イニファータ4と5による重合

4 および 5 は，それぞれ A-B および B-B 型の熱イニファータとして，70～100℃で St や MMA のラジカル重合を誘起（式(4)，(5)）し，7 および 8 のポリマーを生成する。モノ置換エチレンである St の重合はリビング的に進行しないが，1,1 ジ置換エチレンである MMA の重合はリビング的に進行する。MMA では，7，8 の右（h）末端基結合（20）が六置換エタン構造より成り，この結合がラジカル解離することが，モデル化合物を用いた研究から確かめられた。St では五置換エタン構造，また左(t)ポリ St および MMA 末端は四置換エタン構造で，この条件（70～100℃）ではラジカル解離しない。したがって，MMA からのポリマー 7，8 は一官能性高分子イニファータとして作用し，A-B 型ブロック

表1　機能からのイニファータの分類と応用

|	
1）熱イニファータ（熱的に機能するもの）	4, 5 など
2）光イニファータ（光化学的に機能するもの）	5, 6, 21, 22 など
3）高分子イニファータ（高分子に含まれる結合が熱イニファータとして機能するもの）	5, 4 から得られた MMA のポリマーなど（例えば 8 など）
4）高分子光イニファータ（高分子に含まれる結合が光イニファータとして機能するもの）	6, 21, 22 から得られたポリマーなど（例えば 9, 10, 13 など）
5）一官能性イニファータ（高分子の片末端に機能基を導入するもの）	21 など
6）一官能性高分子イニファータ（AB 型ブロックポリマーの合成用）	21 から得られた St のポリマーなど
7）二官能性イニファータ（高分子の両末端に機能基を導入するもの）	22 など
8）二官能性高分子イニファータ（ABA 型ブロックポリマーの合成用）	22 から得られた St のポリマーなど
9）三～多官能性イニファータ（スター，櫛型ポリマー合成用）	23, 25 など
10）多官能性高分子イニファータ（高分子中に多くのイニファータ基を持つもので，スターあるいはグラフト，架橋ポリマーの合成用）	24 など
11）モノマーイニファータ（重合性の二重結合と光イニファータ基を持つもので，マクロマー合成やそれを用いたグラフト共重合体合成用）	25 など
12）高分子ゲルイニファータ（異なるブロック単位を多く持つブロック共重合体の合成用）	26 など

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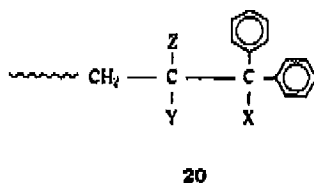
ポリ MMA 末端：Z＝CH₃, Y＝COOH₅, X＝CN or C₆H₅
ポリ St 末端：Z＝H, Y＝C₆H₅, X＝CN or C₆H₅

ポリマーを与える。しかし，リビング性，ブロック
効率はあまり高くない。

5.2　ジチオカルバメート系光イニファータによる重合

4.項で述べたように，6はB-B型の光イニファータであり，6とそれからの生成ポリマー（高分子光イニファータ）9とはイニファータ結合が異なる。これは，高分子設計上好ましくない。加えて，開始反応からくる複雑さを避けるためには，成長末端と同じイニファータ結合のものを用いればよい。次に示すような種々の官能性 A-B 型ジエチル，ジ

官能性　**21**

二官能性　**22**

四官能性（架橋性）　**23**

多官能性（架橋性）　**24**

重合性　**25**　　　　　ゲル型　**26**
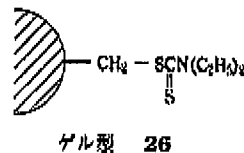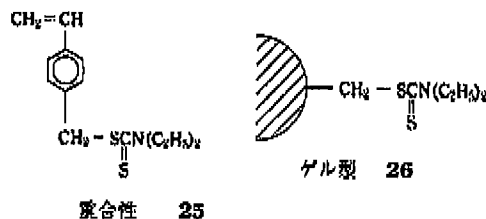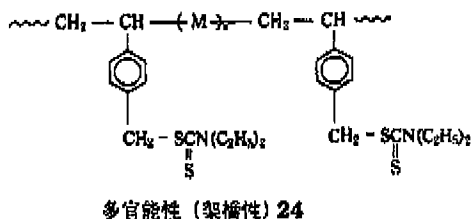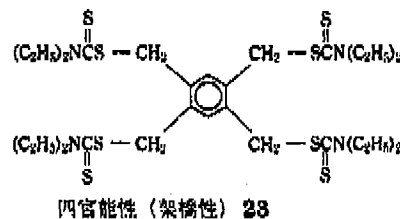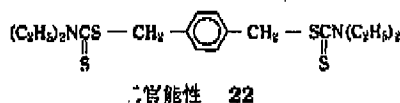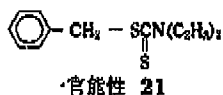
チオカルバメート系光イニファータが合成され，用いられた（機能と応用は表1参照）。

21－26 はいずれも光イニファータとしてリビングラジカル重合を誘起した。例えば，イニファータ結合当たり同じ濃度の21と22を用いてStの重合を行った際の時間ー重合率関係を図1に示す。これから，両者は同じ曲線上にある。分子量はいずれも時間とともに増大するが，二官能性の22では，一官能性の21の2倍となる。同じように四官能性の23ではゲル化の起こることが認められた。ただし，図2に示すように生成ポリマーの分散度は通常のラジカル重合と同程度（$M_w/M_n=2$）であるが，21の場合にはいくらか増大する傾向にあった。また，式(8), (9)で11と12の反応を促進するため6の添加を試みたが，リビング性はいくらか向上するにとどまった。ジチオカルバメート系光イニファータでのB•はチイルラジカルであり，低いながら開始能を持つためと考えられる。この点が，スチレン／ニトロキシド系と異なる。

6.　星型，ブロック，グラフト，架橋ポリマーの設計合成

表1に示したように，種々の官能性ジチオカルバメート系光イニファータを用いることによって上記の各種ポリマーを設計合成することができたが，分子量分布の制御はできなかった。このうち，ブロック，グラフトポリマーの合成については別稿[13]で述べる。

7.　おわりに

これまで種々のイニファータ，とくにジチオカルバメート系光イニファータを用いた高分子合成について述べた。

その結果，各種ポリマーの設計合成[13]が可能となった。最近の成書12)では，一つの章として取り上

げられ，また医用・機器材料へのイニファータ法の応用も進んでいる[13]。

　しかし，現在のジチオカルバメート系光イニファータ法では厳密に式(8)のリビングラジカル重合モデルどおりには機能せず，一部副反応を伴い，結果として分子量分布の規制は不可能であった。これでは精密重合とはいいがたい。近年来のスチレン／ニトロキシド系熱イニファータの使用はStのリビングラジカル重合から単分散に近いポリStの精密合成まで可能となった。これは，また他のリビングイオン重合の活性種をこのイニファータ基に変換し，リビングラジカル重合することによって分子量分布の制御された高分子の精密合成への道を開いた。今後の一層の展開を期待したい。

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13) 本書第2編第3章第2節2.項.

　　　　　　　　　　　　　　　　＜大津　隆行＞

Exhibit B

LIVING RADICAL POLYMERIZATION USING INIFERTER METHOD

1. Introduction

In 1956, Szwarc[1] reported that a living polymer is generated from the polymerization of styrene using sodium naphthalene. The delivery of the living polymerization had a great impact on the control of the primary structure (such as molecular weight, molecular weight distribution, and end group structure) of macromolecules or the design and synthesis of telechelic, block, and graft polymers. Thereafter, the living polymerization was considered as the origin of the structure control, the living of anion polymerization, cation polymerization, radical polymerization, ring-opening polymerization, coordination polymerization, metathesis polymerization, and polycondensation was accomplished from 1970, and the living systems such as group transfer polymerization, immortal polymerization, and new transition metal catalyst polymerization were reported[2)-5)].

The living systems other than the radical polymerization were constructed with the development of a new catalyst system. However, the living radical polymerization could not proceed in a living manner in the presence of a usual catalyst (initiator), because the radical polymerization proceeded via chain reaction while forming electrically-neutral short-lived free radical intermediates as growth-activated radicals. Although there are long-lived free radicals such as DPPH or verdazyl, the radicals serve as polymerization inhibitors and are called stable radicals, which are not the living radicals mentioned herein. The living radical polymerization relates to how to elongate the lifetime of a short-lived radical into a long lifetime. In order to prevent the deactivation of the growth radical by making the mobility of the living radical zero, the polymerization was tried in an emulsion system, a precipitation system, a freezing system, a micro gel system, or a high-viscosity

1

medium.   However, the growth radicals were detected in ESR but the living

polymerization did not proceed in a living manner[2)-8)].

From this point of view, the introduction of a new idea was required to construct

the homogeneous-system living radical polymerization.   In 1982, OTSU et al. suggested

an iniferter method[9)] and a homogeneous-system living radical polymerization model[10)] for

controlling and designing the end group structure of polymers generated by the radical

polymerization.   In recent years, the terms "iniferter" or the "living radical

polymerization" using the iniferter were widely used but often misunderstood.   In this

description, the basic way of thinking thereabout is arranged and the relation thereof to the

recent studies is also described.   The details thereof is referred to in the Introduction[2)-8)].

The design and synthesis of the block and graft polymers will be described in another

document[13)].

As widely known, the radical polymerization is effective for the polymerization of

vinyl monomers and a large amount of general-purpose vinyl polymers are industrially

produced.   However, the control of the molecular weight distribution or the primary

structure (particularly, stereoscopic structure) was not satisfactorily advanced.   In recent

years, the structure analysis of the radical polymerization such as the living radical

polymerization or the precise structure or speed analysis of the growth radicals in the ESR /

pulse laser polymerization have been actively developed.   Accordingly, the advancement

as the precise polymerization method having the merit of radical polymerization is

expected[6)[1]].

2. Iniferter

The radical polymerization is stopped due to the recombination and non-

homogeneousness, and polymers in which initiator pieces are coupled to both ends or one
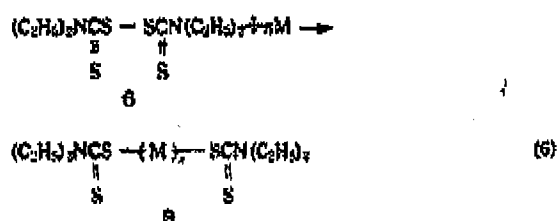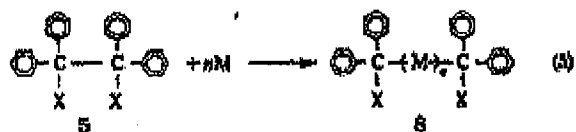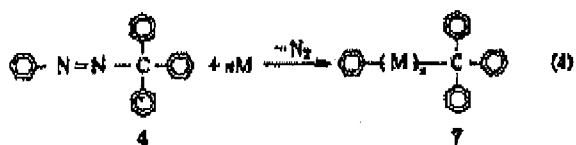
end thereof are produced unless the chain transfer occurs. Since the occurrence of both reactions depends on the monomer structure, it is difficult to control the end group structure of the polymers. If an initiator (R-R) easily causing at least one of the chain transfer to the initiator and the primary radical stop is used, polymers in which pieces of the initiator (R) are coupled to both ends are formed.

$$R-R + nM \longrightarrow R-(M)_n-R \qquad (1)$$

This reaction is only an insertion reaction of monomers into the initiator. The initiator having such a function was named an "iniferter" (abbreviation of initiator-transfer agent-terminator). Formula 2 illustrates the living radical polymerization model described below. The function of telogen (chain transfer agent) in telomerization results from the insertion reaction of monomers. For example, when CCl_4 is used as telogen, the reaction shown by Formula (3) occurs.

$$Cl_3C-Cl + nM \longrightarrow Cl_3C-(M)_n-Cl \qquad (3)$$
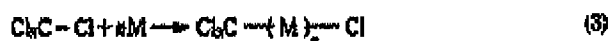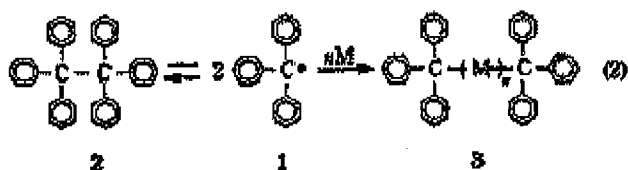
An iniferter used in 1982 was a sulfur compound such as phenyl azotriphenyl methane (4), tetraphenyl ethane ($X=C_2H_5$, CN, OC_6H_5, or the like) (5), or tetraethyl thiuram disulfide (6)[8)7)]. The former two compounds serve as a thermal iniferter and the latter serves as an optical iniferter.

3

$$\text{(O)}-N=N-\overset{\overset{\text{O}}{\|}}{\underset{\overset{\|}{\text{O}}}{C}}-\text{(O)} + n\text{M} \xrightarrow{-N_2} \text{(O)}-(M)_{\overline{n}}-\overset{\overset{\text{O}}{\|}}{\underset{\overset{\|}{\text{O}}}{C}}-\text{(O)} \qquad (4)$$

$$\overset{}{\underset{4}{}} \qquad\qquad\qquad\qquad \overset{}{\underset{7}{}}$$

$$\text{(O)}-\overset{\overset{\text{O}}{\|}}{\underset{X}{C}}-\overset{\overset{\text{O}}{\|}}{\underset{X}{C}}-\text{(O)} + n\text{M} \longrightarrow \text{(O)}-\overset{\overset{\text{O}}{\|}}{\underset{X}{C}}-(M)_{\overline{q}}-\overset{\overset{\text{O}}{\|}}{\underset{X}{C}}-\text{(O)} \qquad (5)$$

$$\overset{}{\underset{5}{}} \qquad\qquad\qquad\qquad \overset{}{\underset{8}{}}$$

$$(C_2H_5)_2NCS-SCN(C_2H_5)_2 + n\text{M} \longrightarrow$$

$$\overset{\|}{\underset{S}{}}\quad\overset{\|}{\underset{S}{}}$$

$$\overset{}{\underset{6}{}}$$

$$(C_2H_5)_2NCS-(M)_{\overline{n}}-SCN(C_2H_5)_2 \qquad (6)$$

$$\overset{\|}{\underset{S}{}}\qquad\overset{\|}{\underset{S}{}}$$

$$\overset{}{\underset{9}{}}$$

Here, it was also discovered that the end groups of the produced polymers (4) to (6) serve as the thermal or optical iniferter (referred to as macromolecule iniferter). The iniferter bond in each case is C-C (trityl), C-C (diphenyl methyl), or C-S bond. In recent years, the iniferter bond in the living system of styrene/nitroxide is $C(C_6H_5)$-ON- bond[11]. The reaction is the insertion reaction of monomer thereto. By polymerizing a second monomer using the polymer iniferter, various block polymers are produced. For example, 10 are obtained from 9.

$$9 + m\text{M}' \xrightarrow{h\nu} \overset{C_2H_5}{\underset{C_2H_5}{}}\!\!N-\overset{}{\underset{\overset{\|}{S}}{C}}-S-(M)_{\overline{n}}-(M')_{\overline{m}}-S-\overset{}{\underset{\overset{\|}{S}}{C}}-N\!\!\overset{C_2H_5}{\underset{C_2H_5}{}} \qquad (7)$$
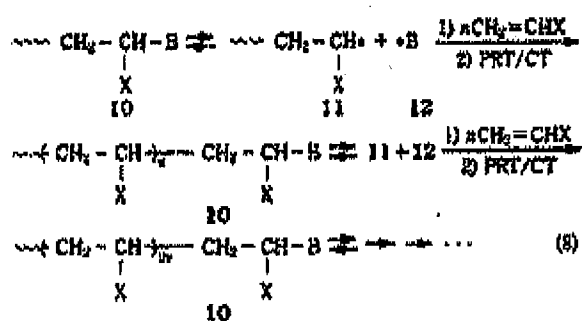
$$\overset{}{\underset{10}{}}$$
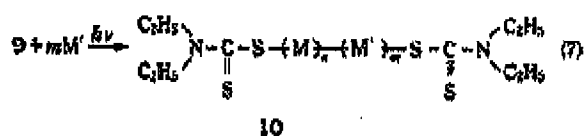
In this way, functional, telechelic, block, or graft polymers are designed and synthesized by using various iniferters.
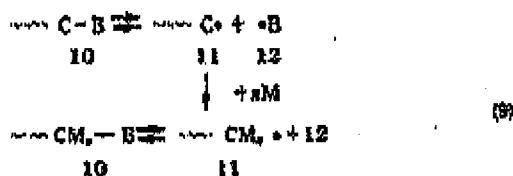
3. Homogeneous Living Radical Polymerization Model

As shown in Formulas 2 and 4 to 7, when monomers are incorporated in the

4

iniferter bonds in radical polymerization, the radical polymerization proceeds in a living manner. The insertion of monomers occurs with the dissociation of the iniferter bonds, the addition of monomers, or the primary radical termination (PRT). The homogeneous living radical polymerization model using the iniferter suggested in 1982 is expressed by Formula 8. Here, CT is a chain transfer to the iniferter bond (C-B) and the reaction is not associated with the model expressed by Formula 8.

$$
\sim\sim CH_2-\underset{\underset{10}{X}}{\overset{|}{C}H}-B \;\rightleftharpoons\; \sim\sim CH_2-\underset{\underset{11}{X}}{\overset{|}{C}H}\bullet \;+\; \bullet B \;\underset{2)\ PRT/CT}{\overset{1)\ nCH_2=CHX}{\xrightarrow{\hspace{1.5cm}}}}\; 12
$$

$$
\sim\sim(CH_2-\underset{\underset{}{X}}{\overset{|}{C}H})_{\!n}\!\!-CH_2-\underset{\underset{10}{X}}{\overset{|}{C}H}-B \;\rightleftharpoons\; 11+12 \;\underset{2)\ PRT/CT}{\overset{1)\ nCH_2=CHX}{\xrightarrow{\hspace{1.5cm}}}}
$$

$$
\sim\sim(CH_2-\underset{\underset{}{X}}{\overset{|}{C}H})_{\!m}\!\!-CH_2-\underset{\underset{10}{X}}{\overset{|}{C}H}-B \;\rightleftharpoons\; \cdots\cdots \qquad (8)
$$

Here, 11 and 12 are produced by the dissociation of C-B bond of 10. 11 is a growth radical which reacts with M. 12 does not have an initiation function in principle, but reacts with only 11 to return to 10, as shown by Formula 9.

$$
\underset{10}{\sim\sim C-B} \;\rightleftharpoons\; \underset{11}{\sim\sim C\bullet} \;+\; \underset{12}{\bullet B}
$$
$$
\Big\downarrow \; +nM \qquad\qquad (9)
$$
$$
\underset{10}{\sim\sim CM_n-B} \;\rightleftharpoons\; \underset{11}{\sim\sim CM_n\bullet} \;+\; 12
$$

Thus, the C-B bond of 10 is a polymer iniferter deemed as a dormant seed of 11. When polymerization occurs in this model, the molecular weight increases with time (polymerization rate) (FIG. 1), and the produced polymer may be used to synthesize block polymers or the like. An example thereof is the living radical polymerization of styrene (St) or methyl methacrylate (MMA) using 4 to 6 as iniferter.
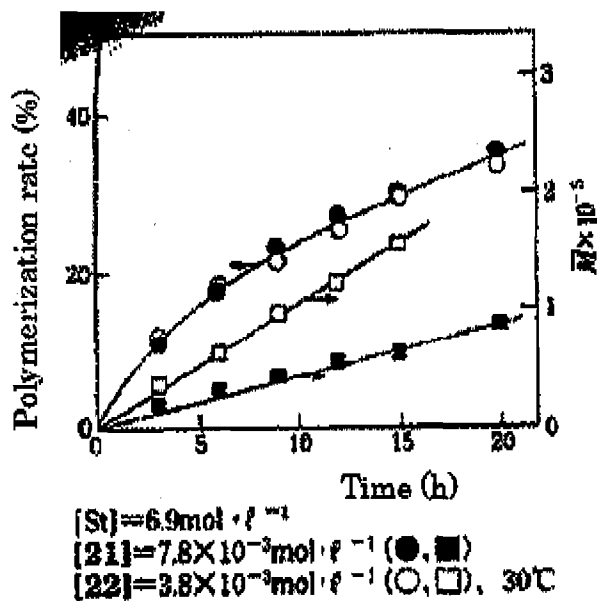
5

FIG. 1 Relations between the time-polymerization rate and between time and molecular weight in photopolymerization of St using 21 and 22

Although these polymerizations are coincident with living ion polymerization in terms of the increase in molecular weight of the produced polymers and the production of the block polymers, the molecular weight distribution is not close to mono-dispersion (see FIG. 2).
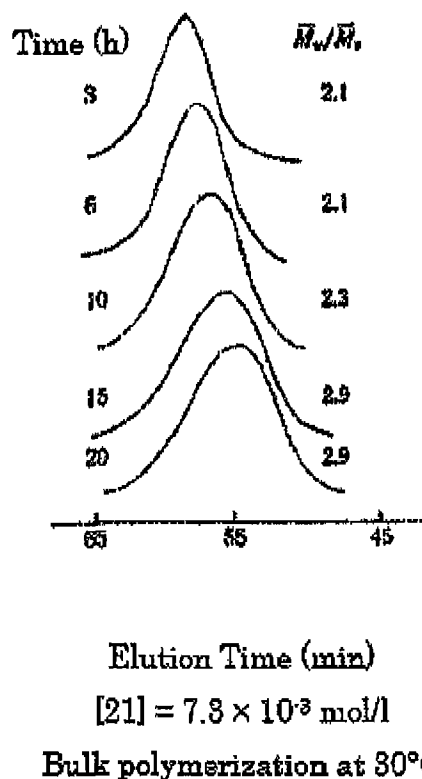
Time (h) $\bar{M}_w/\bar{M}_n$
3   2.1
6   2.1
10   2.3
15   2.9
20   2.9

65   55   45

Elution Time (min)

[21] = 7.3 × 10⁻³ mol/l

Bulk polymerization at 30°C

FIG. 2   GPC curve of polystyrene (St) obtained by photopolymerization using 21

In the ion polymerization, the initiation reaction occurs rapidly in comparison with the growth reaction and no bimolecular termination occurs. In contrast, the initiation reaction is slow, the growth reaction is rapid, and the bimolecular termination also easily occurs in accordance with the increase in concentration of 11 in the radical polymerization. Accordingly, the structure control in the radical reaction requires that the reaction is carried out at a low temperature to enhance the selectivity of 11. Since the thermal iniferters such as 4 or 5 triggers the polymerization at 70°C to 100°C, the substitution of 11 and B in benzene nucleus occurs as the side reaction and the living property is deteriorated. Sine the polymerization using the sulfur-based photo-iniferter (~~C-S) such as 6 proceeds at a room temperature, the side reaction can be avoided. However, since the reaction of 11 and

7

B · (PRT) proceeds slowly in comparison with the (growth) reaction of 11 and M of Formula 9, the growth reaction proceeds in chains and the polymers close to the mono-dispersion cannot be obtained.

In 1994, Georges et al.[11] synthesized poly St with M_w/M_n=12.7 by heating 2,2,6,6,-tetramethylpeperidinyl-1-oxyl (TEMPO), benzoil peroxide, and St at 95°C for 3.5 hours and polymerizing them at 123°C for 69 hours. The iniferter bond (C(C_6H_5)-ON-) is produced in the first stage of the reaction and a St monomer is inserted into the bond. Although the bond has high bonding-dissociation energy, the reaction at 123°C for 69 hours exceeds the expectation, the side reaction is hindered in structure, and B · is a stable radical (inhibitor). Accordingly, it is considered that the condition for the living radical polymerization is satisfied and thus the production of the polymer (here, poly St) exhibiting approximate mono-dispersion is realized by the radical polymerization. A lot of researchers are currently dedicated to the study and new developments are expected[6]-[8].

4. Iniferter Method and Functional Classification and Application thereof

The method for designing an end group structure of a polymer and designing a block polymer using an iniferters is called the iniferter methods. A sulfur-based photo-iniferter method will be described below.[2]-[1]

The iniferters are functionally classified into two types of A-B and B-B.

$$A-B \rightleftharpoons A\cdot + \cdot B \xrightarrow{nM} A-(M)_n-B$$
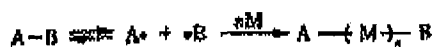
Here, A · is a high-reactive radical and B · is a non- (or low-) reactive radical, where contribute to the initiation and termination, respectively.

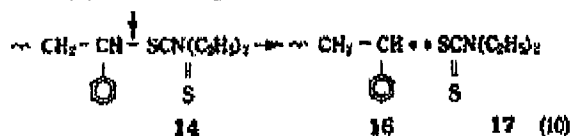$$B-B \rightleftharpoons B\cdot + \cdot B \xrightarrow{xM} B-(M)_x-B$$

Here, B · is a low-reactive radical and contributes both the initiation and termination reactions. When St is polymerized using disulfide 6 of the B-B type as the

photo-iniferter, polymer 13 is produced.

$$(C_2H_5)_2NCS \cdot CH_2 \cdot CH \left(CH_2 - CH \right)_{n-2} CH_2 - CH \cdot SCN(C_2H_5)_2$$
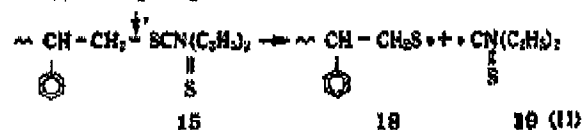
13
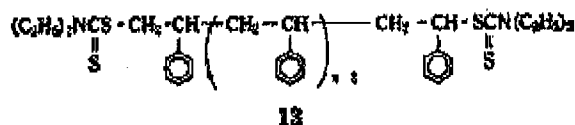
Iniferter groups are coupled to both ends of 13. However, the end group structures 14 and 15 are different from each other in terms of the previous monomer unit, and the bonding positions to be photodissociated. That is,

Right (h) end group:

~ CH$_2$ - CH $\cdot$ SCN(C$_2$H$_5$)$_2$ → ~ CH$_2$ - CH $\cdot$ + $\cdot$ SCN(C$_2$H$_5$)$_2$

14 **16** **17 (10)**

Left (t) end group:

~ CH - CH$_2$ $\cdot$ SCN(C$_2$H$_5$)$_2$ → ~ CH - CH$_2$S $\cdot$ + $\cdot$ CN(C$_2$H$_5$)$_2$

15 . **18** **19 (11)**

If a bonding of 14 shown by the arrow is dissociated, polystyryl radical 16 as the growth radical 11 is reproduced from the end of 14 and low-reactive thiyl radical 17 is produced at the same time. Low-reactive polyphenylethyl thiyl radical 18 and high-reactive carbon radical 19 are produced from the end of 15 and 11 is not reproduced. Accordingly, this is not suitable to design the end structure, and the iniferter of A-B type by which 11 is necessarily reproduced should be used. In general, the living property and the block efficiency of the A-B type are higher.

The classification of iniferters in view of functionality and application is shown in Table 1.

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Table 1 Classification and Application of Iniferters in view of Functionality

1	Thermal Iniferter (thermally functioning)	4, 5, or the like.
2	Photo-iniferter (photochemically functioning)	5, 6, 21, 22, or the like.
3	Polymer iniferter (bond of polymer functions as a thermal iniferter)	MMA polymers (such as 8) obtained from 5 or 4, or the like.
4	Polymer iniferter (bond of polymer functions as a phot-iniferter)	Polymers (such as 9, 10, or 13) obtained from 6, 21, or 22, or the like.
5	Mono-functional iniferter (functional group is introduced into one end of a polymer)	21, or the like.
6	Mono-functional polymer iniferter (for synthesis of AB type block polymer)	St polymers obtained from 21, or the like.
7	Bi-functional iniferter (functional groups are introduced into both ends of a polymer)	22, or the like.
8	Bi-functional polymer iniferter (for synthesis of ABA type block polymer)	St polymers obtained from 22, or the like.
9	3 or more functional iniferter (for synthesis of star or comb type polymer)	23, 25, or the like.
10	Multi-functional polymer iniferter (having many iniferter groups in a polymer and available for synthesis of star, graft, or cross-linking polymers)	24, or the like.
11	Monomer iniferter (having a polymeric double bond and photo-iniferter group and available for synthesis of a macromer or synthesis of a graft copolymer using it)	25, or the like
12	Polymer gel iniferter (for synthesis of a block copolymer having many different block units)	26, or the like.

5. Features of a Living Radical Polymerization using an Iniferter

5.1 Polymerization using Thermal Iniferters 4 and 5

Thermal iniferters 4 and 5 are A-B type and B-B type of thermal iniferters,

respectively, and trigger the radical polymerization of St or MMA at 70°C to 100°C (Formulas 4 and 5), and produce polymers 7 and 8. The polymerization of St which is a mono-substituted ethylene does not proceed in the living manner, but the polymerization of MMA which is a 1,1-di-substituted ethylene proceeds in the living manner. The study using the model compounds demonstrated that the radical dissociation of the right (h) end group bond (20) of 7 or 8 having a 6-substituted ethane structure occurred in MMA. The radical dissociation of St having a 5-substituted ethane structure, or a left (t) poly St or MMA ends having a 4-substituted ethane structure did not occur at 70°C to 100°C. Accordingly, the polymers 7 and 8 obtained from MMA serve as mono-functional polymer iniferters and give the A-B type block polymers. However, the living property and the block efficiency are not high.
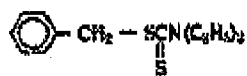

20
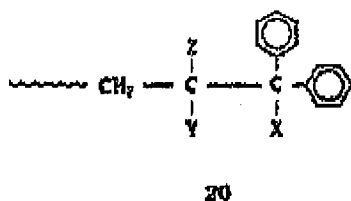
Poly MMA end: Z=CH$_3$, Y=COOH, X=CN or C$_6$H$_5$

Poly St end: Z=H, Y= C$_6$H$_5$, X=CN or C$_6$H$_5$

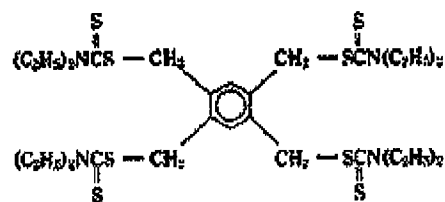### 5.2 Polymerization using Dithiocarbamate Photo-Iniferter

As described above, 6 is a B-B type photo-iniferter, and 6 and polymer (polymer photo-iniferter) 9 produced therefrom are different in iniferter bond. This is not desirable for polymer design. In addition, in order to avoid the complication resulting from the initiation reaction, the same iniferter bond as that of the growth end can be used. Various functional A-B type diethyl and dithiocarbamate-based photo-iniferter described below were synthesized and used (see Table 1 for the functions and applications).
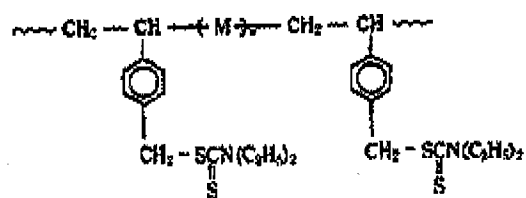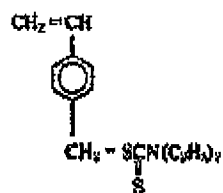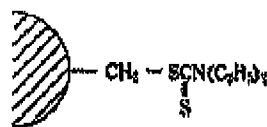
11

$\bigcirc$— CH$_2$ — SCN(C$_2$H$_5$)$_2$
‖
S

Mono-functional 21

(C$_2$H$_5$)$_2$NCS — CH$_2$ —$\bigcirc$— CH$_2$ — SCN(C$_2$H$_5$)$_2$
‖   ‖
S   S

Bi-functional 22

S   S
‖   ‖
(C$_2$H$_5$)$_2$NCS — CH$_2$ CH$_2$ — SCN(C$_2$H$_5$)$_2$

(C$_2$H$_5$)$_2$NCS — CH$_2$ CH$_2$ — SCN(C$_2$H$_5$)$_2$
‖   ‖
S   S

Tetra-functional (cross-linking) 23

～ CH$_2$ — CH —(M)$_n$— CH$_2$ — CH ～

$\bigcirc$ $\bigcirc$

CH$_2$ – SCN(C$_2$H$_5$)$_2$ CH$_2$ – SCN(C$_2$H$_5$)$_2$
‖   ‖
S   S

Multi-functional (cross-linking) 24

CH$_2$=CH

$\bigcirc$

CH$_2$ – SCN(C$_2$H$_5$)$_2$
‖
S

Polymerized 25

$\text{CH}_2 - \underset{\underset{S}{\parallel}}{S}CN(C_2H_5)_2$

Gelated 26

21 to 26 are all photo-iniferters and triggered the living radical polymerization. For example, the time-polymerization relation is shown in FIG. 1 where the polymerization of St was carried out using 21 and 22 having the same concentration per iniferter bond. Both can be seen in the same curve. The molecular weight increases with time, but the molecular weight of 22 having bi-functionality is double that of 21 having mono-functionality. Similarly, it was observed that the gelation occurs in 23 having tetra-functionality. However, as shown in FIG. 2, the degree of dispersion of the produced polymer is similar to that of the usual radical polymerization ($M_x/M_n=2$), but tends to increase to only some extent in 21. The addition of 6 was tried to promote the reaction of 11 and 12 in Formulas 8 and 9, but the living property was improved to some extent. This is probably because B · in the dithiocarbamate-based photo-iniferter is thiyl radical and has a low initiation function. In this point, the dithiocarbamate-based photo-iniferter differs from a styrene/nitroxide iniferter.

6. Design and Synthesis of Star, Block, Graft, and Cross-linking Polymers

As shown in Table 1, various polymers described above could be designed and synthesized by using various functional dithiocarbamate photo-iniferters, but the molecular weight distributions thereof could not be controlled. The synthesis of block and graft polymers would be described in another document[13].

7. Conclusion

The synthesis of polymers using various iniferters, particularly, a dithiocarbamate-based photo-iniferter, has been described above.

As a result, the design and synthesis[13] of various polymers were possible. The iniferter method was treated as one chapter in recent written reports12) and the application of an iniferter method to medical instrument materials has advanced[13].

However, strictly speaking, the living radical polymerization model of Formula 8 does not function in the present dithiocarbamate-based photo-iniferter method and the control of the molecular weight distribution was not possible as the result of some side reactions. This cannot be said as precise polymerization. The recent use of styrene/nitroxide thermal iniferter enabled the living radical polymerization of St and the precise synthesis of poly St exhibiting an approximate mono-dispersion. It opens the road to the precise synthesis of polymers of which the molecular weight distributions are controlled by converting the radicals of other living ion polymerization into the iniferter groups to polymerize the living radicals. Further development is expected in the future.

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